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# Preparation and Characterization of PC and SAN Composites and PC/SAN Blends with Graphene Nanofiller

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# PREPARATION AND CHARACTERIZATION OF PC AND SAN COMPOSITES AND PC/SAN BLENDS WITH GRAPHENE NANOFILLER

By

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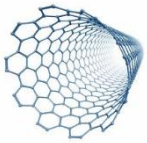

Leibniz-Institut
für Polymerforschung
Dresden e. V.

# Preparation and characterization of PC and SAN composites and PC/SAN blends with graphene nanofiller

*Marc-Olivier Blais*

# Contents

## Contents

# Acknowledgement

I would like to thank the following people for their help and kind advice during this project:

- Mr. Marco Liebscher: As my mentor and primary contact in Dresden, he helped me become settled in Germany and guide the direction of this project.
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- Mrs. Ulrike Jentzsch-Hutschenreuther: Mrs. Jentzsch-Hutschenreuther was quite helpful with the preparation of samples.

# Project Summary

For my thesis defense I plan to focus on both the scientific merit of my research and a reflection of what I personally gained from my experience in Germany. The central goal of this scientific study was to prepare a polymer blend with fine co-continuous blend morphology which contains well dispersed graphene nanofiller. Graphene is currently of great interest as a filler within the polymer nanocomposite community due to its excellent electrical conductivity, favorable mechanical properties, and high surface area. The polycarbonate (PC)/ Poly (styrene acrylonitrile) (SAN) blend system is of interest due to their ubiquitous use in both industrial and consumer applications and therefore we intend to incorporate graphene into this system. The selective localization behavior of carbon fillers in polymer blend systems has historically been of interest and to this end we qualitatively assessed the dispersion and localization of graphene nanofiller within PC/SAN blends systems as well as the transfer kinetics of the graphene between the two polymer phases.

My reflection will focus on how this experience helped me understand how I want to live my life in the near future both personally and professionally. I realized that I will be much happier working at the intersection of engineering and management rather than working within a research setting. I have also learned that I want live and work abroad for an extended period of time. I would not have been able to obtain or even appreciate the position I will fill upon graduation without the knowledge and wisdom I gained in Dresden.

# I. Personal Significance

I was groggily staring at my phone. It was late morning and the shades had been left open from the night before. The Florida sun was a bit too much for my eyes … such is life during spring break at Daytona Beach. It was early March 2012 and the email I had just received was helping me ignore my hangover. I had been accepted. Marco Liebscher and his supervisor, Petra Pötschke, had been pleased with my profile and were inviting me to Dresden for the summer to aid in scientific research. To be honest, in that moment I was filled with doubt. I had never been away from my family for any extended period of time, seeing as they live in Columbia. Not only would I be away from any one I cared about or knew, I would be in a foreign country immersed in a language I still do not understand to this day. I experienced doubt, I felt fear, I felt the temptation of making an easier call and falling back on some domestic summer opportunities I had been offered. It was this fear and this doubt that made me do it. On May 16th, 2012 I boarded a transatlantic flight in Charlotte, NC and I now know that I made a wonderful decision.

I learned about the DAAD (German Academic Exchange Service) through one of my older classmates who had participated in the program the previous year. When I was applying to the program I was not fully appreciative of its significance: a research internship while living abroad. At the time I was not aware of what such an experience would mean for my personal development as well as my professional marketability. When I arrived in Dresden I was greeted with a collage of sun and rain, which would become a typical day in Germany as I would soon learn. The research department in which I was working was a mixture of different countries: Turkey, South Africa, France, Spain, Germany, Poland, and now US.

I quickly became friends with a French student, Jerome, who was at Leibniz for a similar internship. As he helped me with my French and I his English I immediately came to a realization that is in addition to the obvious value of gaining international experience. I came to the realization that if I remain in the United States after university and work in a mainly Anglophone setting I will begin to lose touch with my francophone roots and my maternal

language. Yes, I could simply read French books, listen to French media, and browse French websites, yet I would still live and think in English. At the time, I realistically saw myself working in a francophone setting soon after college. I have since expanded my scope of desired working environments, realizing that there is value in learning a third language as well. It is clear to me, from my time in Germany, that working in monolingual environment for an extended period of time would not satisfy me. This is one of the reasons I have chosen my current career path.

I could go on and say that this experience gave me the chance to appreciate working in diverse teams, overcoming cultural and language barriers, and to sharpen my professional discipline. Yes, all of these things are true and I understand their importance. However, my time in Dresden taught me a valuable lesson: I dislike working solely within the confines of a laboratory. This was not a realization that I had never come across in the past; Dresden simply confirmed my suspicions. I found the social environment, pace of work, and task variety which encompass scientific research to be unpleasant. I enjoy interacting with people not only of various cultural backgrounds, but also of various educational and social backgrounds. At Leibniz I was spending the majority of my time with people who had equivalent or greater levels of education. Additionally, these people were mainly from engineering or pure sciences backgrounds. My later experience as an intern in a manufacturing plant made me realize that I enjoy the challenge of working with educationally and socially diverse teams. The real challenge was not communicating with the finance or accounting associates. The hard part was working with line operators on the factory floor. In the end, the hard part was also the fun part.

The pace of work in thorough scientific research is slow, from my point of view. Monumental paradigm shifts are rare and I fail to find the immediate societal impact of the work being conducted. Many may call me impatient or short-sighted, yet I know that I gain the most satisfaction from working on projects which have relative immediate impact on my colleagues and society (in industry, the customer more directly). Again, my experience later in industry allowed me to experience the phenomenon of immediate impact and urgency. My

projects would immediately save time for the operators and augment their convenience, which would in turn save the company money.

When I mention task variety I am referring to the need to switch between individualistic technical tasks to more socially collaborative tasks. While it is true that this can occur in scientific research, it would seem that the frequency of switching between tasks is lower. In the factory a typical day consisted of work at my desk, computer station, at staff meetings, on the manufacturing lines, in the quality lab, meeting managers, and coordinating with external contractors. My time in Dresden consisted of desk work and lab work, with some moments spent collaborating within the department and team. My propensity for experiencing boredom was an important contributor to my dislike of academic research.

Dresden, without a doubt, also taught me a lesson about realizing what I truly adored: *living* in an alien environment. It was especially interesting to realize that people anywhere in the world live their mundane lives just like I do back home. My previous experiences in Europe had been short leisurely trips which left me with the subconscious sense that Western Europe is full of fairies and castles, to put it frankly. Of course, appreciating a foreign culture from an intellectual standpoint is normal and even necessary if you want to develop an understanding of a region. However, developing true respect only comes with living, buying groceries, paying rent, and paying taxes in said area. I want to complain about French politics like the French, German politics like the Germans, and Italian politics like the Italians. I want to experience the burden of doing my job while learning and struggling with the language. I do not want to visit a foreign country, I want to live it.

These realizations helped me seek and obtain my current employment opportunity beginning after graduation. I have secured a place in the 2014 Prysmian Group Graduate Program. This program will allow me to pursue an immediate international career whilst rotating between different business units and functions. I had other opportunities at my disposal and chose this particular one because of one thing: uncertainty. Approximately one year after graduation I could either be working in Milan, Italy or Sao Paulo, Brazil or

anywhere in-between. I could be working in R&D, quality, process engineering, logistics, application engineering, or something else. I knew going in that this would not be an easy role to fill … and that is why I chose it.

# II. Objective

The central goal of this study was to prepare a polymer blend with fine co-continuous blend morphology which contains well dispersed graphene nanofiller. Graphene is currently of great interest as a filler within the polymer nanocomposite community due to its excellent electrical conductivity, favorable mechanical properties, and high surface area. The polycarbonate (PC)/ Poly (styrene acrylonitrile) (SAN) blend system is of interest due to their ubiquitous use in both industrial and consumer applications and therefore we intend to incorporate graphene into this system. The selective localization behavior of carbon fillers in polymer blend systems has historically been of interest and to this end we will qualitatively assess the dispersion and localization of graphene nanofiller within PC/SAN blends systems as well as the transfer kinetics of the graphene between the two polymer phases. To achieve this goal, this study produced both homopolymer and polymer blend systems. Initially, a set of samples was created which consisted of homopolymers (PC or SAN) containing graphene with appropriately adjusted weight loadings. These samples were used to assess the effect of different mixing parameters on the dispersion and agglomeration of the graphene. Three blend systems were also produced which consisted of PC (60wt%), SAN (40wt%), and xGnP5 (1wt%). These three systems were used to qualitatively assess the transfer kinetics of the graphene between the two phases. The optimally dispersed sample from the homopolymer set was then incorporated with the partner polymer to produce the final PC (60wt%), SAN (40wt%), and xGnP5 (1wt%) blend product.

# III. State of Art

Graphene is a two-dimensional allotrope of carbon with a molecular structure typically resembling that of graphite with sp2 hybridized carbon atoms configured in a repeating aromatic ring structure. Due to its high aspect ratio graphene has impressive mechanical and electrical properties with a Young's modulus of up to 1TPa and an electrical conductivity of up to 6000S/cm. These properties, which are up to par with that of CNTs, make graphene an interesting possibility as a nanofiller in polymer systems. Graphene can be produced from graphite in a top-down process or in a bottom-up process involving chemical vapor deposition or epitaxial growth on SiC.[1] For use in polymer nanocomposites, a top-down approach is favored due to the need of large amounts of graphene filler. The most common method involves producing thermally reduced graphene (TRG), also referred to as functionalized graphene sheets (FGS). [1,2]

TRG is produced by oxidizing raw graphite usually via the introduction of powerful oxidants with the presence of nitric or sulfuric acid. The graphite is now called graphite oxide (GO) and consists of carbon sheets with an interlayer spacing of 6 to 10 angstroms. These sheets are believed to be interspersed with epoxide, ketone, and hydroxyl groups. Chemically modified graphene can be produced from GO through chemical or thermal means. The resulting graphene cannot be called *pristine* due to the always present chemical defects owing to the incomplete reduction process. For use in polymer nanocomposites, TRG is preferred since it can be produced in large quantities with relative economic feasibility. The thermal reduction process typically involves exposing GO to 1000°C in an inert atmosphere for 30 seconds. Exfoliation occurs due to the decomposition of epoxy and hydroxyl sites and the subsequent release of $CO_2$ gas. Exfoliation leads to 30% weight loss through the loss of oxygen groups and water while a volume expansion of 100-300 times is also seen.[1]

Within the last decade an exceeding number of studies have incorporated graphene and its derivatives into homopolymer systems using a variety of preparation methods such as solvent and melt mixing. This present study only focuses on melt mixing in PC, SAN, and PC/SAN blends, therefore only literature pertaining to these materials and techniques will be

examined. Melt mixing is being investigated in this study since it is a popular method for preparing the thermoplastic polymers being used, polycarbonate (PC) and poly(styrene acrylonitrile) (SAN) due to its high throughput and ability to produce large quantities of product.[7] Shen et al. showed that melt mixing of polypropylene(PP)/graphene systems with a twin-screw compounder can indeed be used to modify the dispersion and exfoliation of graphene. They found that with increasing mixing time the delamination and dispersion of the graphene improves.[8] Wakabayashi et al. used a similar PP/graphite system in a process known as solid-state shear pulverization (SSSP).[9] SSSP is a modified form of melt mixing in which strong shear and compressive forces are carefully applied to the melt system. Wakabayashi found an improvement in graphite dispersion when using this process as compared to conventional melt mixing.[9] Drzal et al. , prepared graphite nanoplatelet/LLDPE (linear low density polyethylene) using various twin-screw microcompounding regimes. It was found that solution mixing showed better dispersion of graphite than melt mixing and that counter-rotating screws also created the best graphite dispersion.[10] Studies has also been conducted which incorporated graphene into PC and SAN individually. Functionalized graphene sheets have been melt mixed with PC and have been shown to exfoliate upon mixing. FGS filled PC had markedly lower concentration thresholds (0.5wt%) than that filled with graphite (~4wt%).[11] Thermally reduced graphite oxide, TrGO, was found to disperse quite well in PC and in SAN by using a solvent + melting blending method. Exfoliation of the TrGO was seen with aspect ratios of >200. TrGO was found to have improved electrical and thermal properties in PC and SAN when compared to bulk graphite.[12]

Polymer blend systems are of current industrial and scientific interest due to the ability to tailor the properties of the final blend by combining the effects, in some cases synergistically, of two initial homopolymers.[4,5] Blend systems have also drawn interest as hosts for carbon nanofillers such as CNTs and graphene. Vleminckx looked at graphene nanoplatelets incorporated into Poly[(r-methylstyrene)-co-(acrylonitrile)/poly(methyl-methacrylate) blends and determined that there is a significant difference in conductivity between monophasic and biphasic melts containing 2wt% TRG, with the latter being highly conductive compared to the former.[5] Potschke et al. incorporated MWCNTs into SAN/PC blends which possessed a co-continuous biphasic morphology.[6] The MWCNTs were shown to

favor localization in either the PC or the SAN phases depending on the addition of a reactive component (RC) in the SAN. [6] Understanding the localization and subsequent formation of percolation networks involving carbon nanofillers is of great importance if electrically useful polymer nanocomposites are to be eventually produced. Additionally, the PC/SAN system resembles the commercially available and used PC/ABS (acryl-butadiene-styrene) system.[6] Even when CNTs were premixed into stock SAN polymer they managed to transfer quite well into the PC phase during blending.[6]Therefore, this study had relevant economic interest as well. To date, no studies have been conducted which explore the localization behavior of graphene nanoplatelets in polymer blend systems nor the transfer kinetics of said graphene and thusly is the crux of this study.

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# IV. Experimental

## Materials:

xGnP Grade M Graphene Nanoplatelets were obtained from XG Sciences, MI,USA. Two batches of xGnP graphene nanoplatelets were used, one with an average diameter of 5µm (GnPM5) and another with that of 25µm (GnPM-25). All nanoplatelets batches had an average thickness of 6-8nm and a density of 2.2g/cc. MWCNTs (NC7000) were obtained from Nanocyl, Belgium with a density of 1.75g/cc. Poly(styrene acrylonitrile) (SAN) (Luran 358N) was obtained from, BASF, Ludwigshafen, Germany and has a density of 1.08g/cc, and polycarbonate (PC) (Makrolon 2600) from Bayer MaterialScience, Germany which has a density of 1.2g/cc.

## Summary of Homopolymer Systems Prepared:

### *Comparison of xGnP M-5 and xGnP M-25*

The following homopolymer samples incorporating either 1 wt % GnPM5 or GnPM25 were prepared at mixing temperature of 260°C, screw speed of 100rpm, and a mixing time of 5minutes.

1. GnPM-5(1wt%) / PC
2. GnPM-25 (1wt%) /PC
3. GnPM-5(1wt%) / SAN
4. GnPM-25(1wt%) / SAN

## *Comparison of different melting conditions with xGnP M-5*

The following homopolymer samples incorporating GnPM-5 were prepared under various mixing temperatures, compounder screw speeds, and times:

1. (1.68 wt% GnPM-5/PC – premix) : 260°C, 250 rpm, 5 min
2. (1.68 wt% GnPM-5/PC – premix) : 260°C, 250 rpm, 15 min
3. (1.68 wt% GnPM-5/PC – premix) : 260°C, 100 rpm, 15 min
4. (1.68 wt% GnPM-5/PC – premix) : 260°C, 100 rpm, 5 min
5. (2.53 wt% GnPM-5/SAN – premix) : 260°C, 250 rpm, 5 min
6. (2.53 wt% GnPM-5/SAN – premix) : 260°C, 250 rpm, 15 min
7. (2.53 wt% GnPM-5/SAN – premix) : 260°C, 100rpm, 15 min
8. (2.53 wt% GnPM-5/SAN – premix) : 260°C, 100rpm, 5 min

The intent of producing these samples was to determine both the mixing conditions and homopolymer which would result in optimal dispersion and minimal agglomeration of graphene. This is desired in order to minimize both the thermal and electrical percolation thresholds for graphene in these systems. The optimized system for both SAN and PC homopolymers would then be incorporated with their partner polymer to create a final blend system consisting of PC (60wt%), SAN (40wt%), and graphene (1wt%).

# Summary of Polymer Blend Systems Prepared:

## *Mixing Conditions 1: 5min, 100rpm*

The following polymer blend systems with a final graphene content of 1wt.% were prepared:

1. GnPM-5(1wt%)/PC(60wt%)/SAN(40wt%)
2. [GnPM-5(1.68 wt%)/PC (60wt%)premix1a]/SAN(40wt%)
3. [GnPM-5(2.53 wt%)/SAN(40wt%) premix1b]/PC (60wt%)
4. MWCNT (1wt%) / PC(60wt%)/SAN(40wt%)

These samples and pre-mixtures were prepared at a temperature of 260°C, with a screw speed of 100 rpm, and a mixing time of 5 minutes. All three of these samples are blend systems consisting of PC (60wt%), SAN (40wt%), and graphene (1wt%). They only differ in the method with which they were prepared. Sample number 1was produced in a single mixing step in which all of the raw materials were added to the micro-compounder at the same time. Samples number 2 and 3 were produced in two steps. First, the graphene was melt mixed with a homopolymer at a slightly higher weight loading. This was done to achieve 1wt% in the final blend. The initial homopolymer composite was then appropriately weighed, vacuum dried at 120°C overnight, and then added with the partner polymer into the micro-compounder under the same mixing conditions. The final blend systems were compared in order to assess the transfer kinetics of the graphene between the PC and SAN phases as well as the relative dispersion and agglomeration of the graphene. CNTs were used as a nanofiller in sample number 4 so as to be used as a reference when assessing the graphene dispersion. Sample 4 was produced in a single step.

## *Premixing Conditions 2: 15 min, 250rpm*

The following optimized blend systems were prepared:

1. [GnPM-5(1.68 wt%)/PC (60wt%)premix]/SAN(40wt%)
2. [GnPM-5(2.53 wt%)/SAN(40wt%) premix]/PC (60wt%)

The homopolymer pre-mixtures were taken from the homopolymer samples prepared at a screw speed of 250rpm and a mixing time of 15minutes. The blend system was created at 260°C, with a screw speed of 100rpm and a mixing time of 5 minutes. These samples were prepared to assess transfer kinetics of the graphene as well as to make an attempt at obtaining the optimal dispersion and agglomeration possible via melt mixing procedures.

## Sample preparation and DSM melt processing:

All raw materials were weighed in a fume hood in ambient conditions and placed in small glass vials which were topped with laboratory tissue. The vialed samples were placed under vacuum at 120°C overnight in order to remove moisture. An Xplorer DSM 15 twin-screw microcompounder was used to prepare the polymer samples via melt mixing. A constant melt temperature of 260°C was used with varying spin speeds or either 250 or 100 rpm, and either a 5 or 15 minute mixing time. In operating the micro-compounder initially the screws are installed and the mixing chamber is properly closed making sure that the exit valve is in the closed position. The chamber is heated to 260°C and the dried materials (12cc) are added via a hand operated hopper. The hopper is removed and replaced with a conforming metal stopper after which the mixing period officially begins. The polymer product is then extruded at the end of the mixing period via the exit valve and the chamber is thoroughly cleaned using a glass based cleaning polymer.

## Optical Microscopy Investigation:

Samples of each polymer system were cut to size using a razor blade. The cut pieces were then inserted into a Leica microtome [need model] and then sectioned into 5μm thick sections using a glass knife room at temperature. The sections were then placed onto a glass slide using agar and a cover slip and subjected to a constant force for several hours in order to assure that the sections are flattened evenly in the agar. Optical micrographs were taken of the sections using a Olympus BH-12 optical microscope at both 4X and 10X magnifications.

## Transmission Electron Microscopy (TEM) Investigation:

The polymer samples were ultra-microtomed into 50nm sections at room temperature. The sections were then placed onto TEM grids. For the microscopy, a Zeiss Libra 200 TEM with an acceleration voltage of 200keV was used.

## Scanning  Electron Microscopy (SEM) Investigation:

The polymer samples were immersed in a 30% NaOH solution at 105°C and refluxed for 30 minutes in order to chemically etch away the PC phase. After the treatment the samples were purged in deionized water to remove residuals from the surface. For the investigations a Zeiss Neon 40 with 1,5 keV acceleration voltage was used.

## Electrical Resistivity Measurements:

Electrical resistivity measurements were conducted using a Keithley 6517a ohmmeter with the polymer samples pressed into circular plates with a diameter of 60mm and an average thickness of 0.50mm. The resistivity was measured along the axis of the pressed disk for the graphene samples and along the longitudinal axis of cut strips for the CNT reference. Pressing was conducted using a Paul Weber PW 40 EH. The following samples were tested for their electrical resistivity:

- GnPM-5(1wt%) / PC
- GnPM-25 (1wt%) /PC
- GnPM-5(1wt%) / SAN
- GnPM-25(1wt%) / SAN
- GnPM-5(1wt%)/PC(60wt%)/SAN(40wt%)
- [GnPM-5(1.68 wt%)/PC (60wt%)premix1a]/SAN(40wt%)
- [GnPM-5(2.53 wt%)/SAN(40wt%) premix1b]/PC (60wt%)
- MWCNT (1wt%) / PC(60wt%)/SAN(40wt%)
- PC(60wt%)/SAN(40wt%)

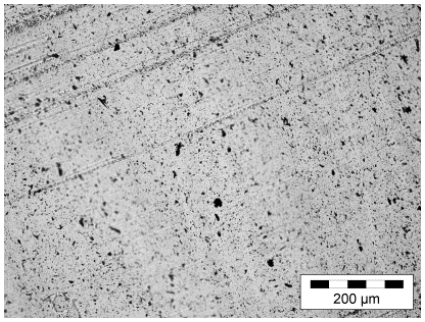
# V. Results

## *Comparison of xGnP M-5 and xGnP M-25*

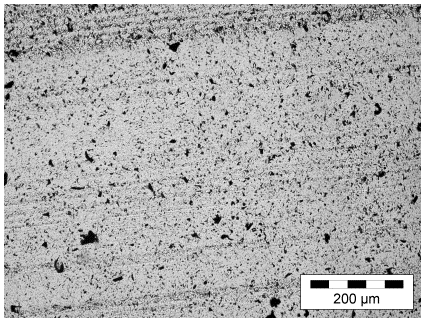
The following optical micrographs (Fig. 1), taken at 10X magnification, show a noticeable difference in the size of the agglomerates between samples incorporating GnPM5 and GnPM-25. The PC and SAN samples incorporating GnPM-5 show smaller agglomerates than the samples incorporating GnPM-25. This is expected owing to the smaller diameter of the GnPM-5 nanoplatelets. Additionally, one can see improved dispersion of the graphene with the PC as compared to the SAN. This is not entirely too surprising since MWCNTs favor dispersion and disperse better in the PC phase[5] and therefore it similar behavior with graphene can be expected.

Figure 1

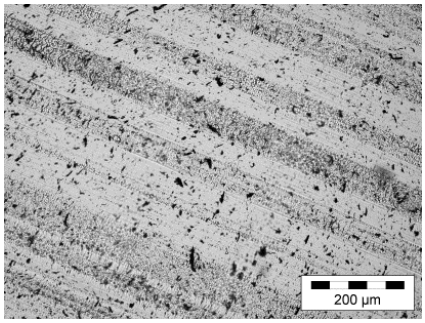
GnPM-5(1wt%)/PC



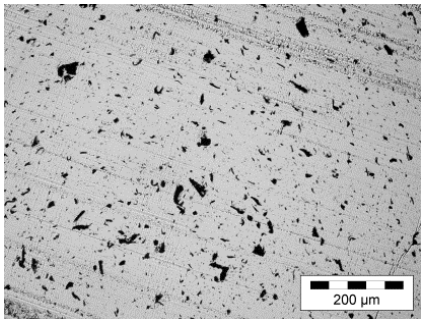

GnPM-25(1wt%)/PC




GnPM-5(1wt%)/SAN




GnPM-25(1wt%)/SAN



## *Comparison of different melting conditions with xGnPM-5*

As referenced in the corresponding experimental section of this report, eight graphene homopolymer composites were created for eventual use in a polymer blend system. Optical micrography (Fig. 2,3) clearly denotes a difference between the use of PC as opposed to SAN as the bulk polymer. Graphene forms visibly smaller agglomerates in PC when compared to SAN. Indeed, in SAN the agglomerates appear quite irregular compared to PC and understandably so when compared to previous literature incorporating CNTs.[5] As the mixing regimes involved increase mixing times and screw speeds the agglomerates appeared to shrink in size for the PC homopolymer samples. The SAN samples do not show conclusive visual evidence of agglomerate size changes due to changing mixing conditions. These observations are clearly seen in figures 2 and 3. The images outlined in red indicate the samples which were further used in the two step polymer blending.

Figure 2 – (2.53 wt% GnPM-5/SAN – premix)

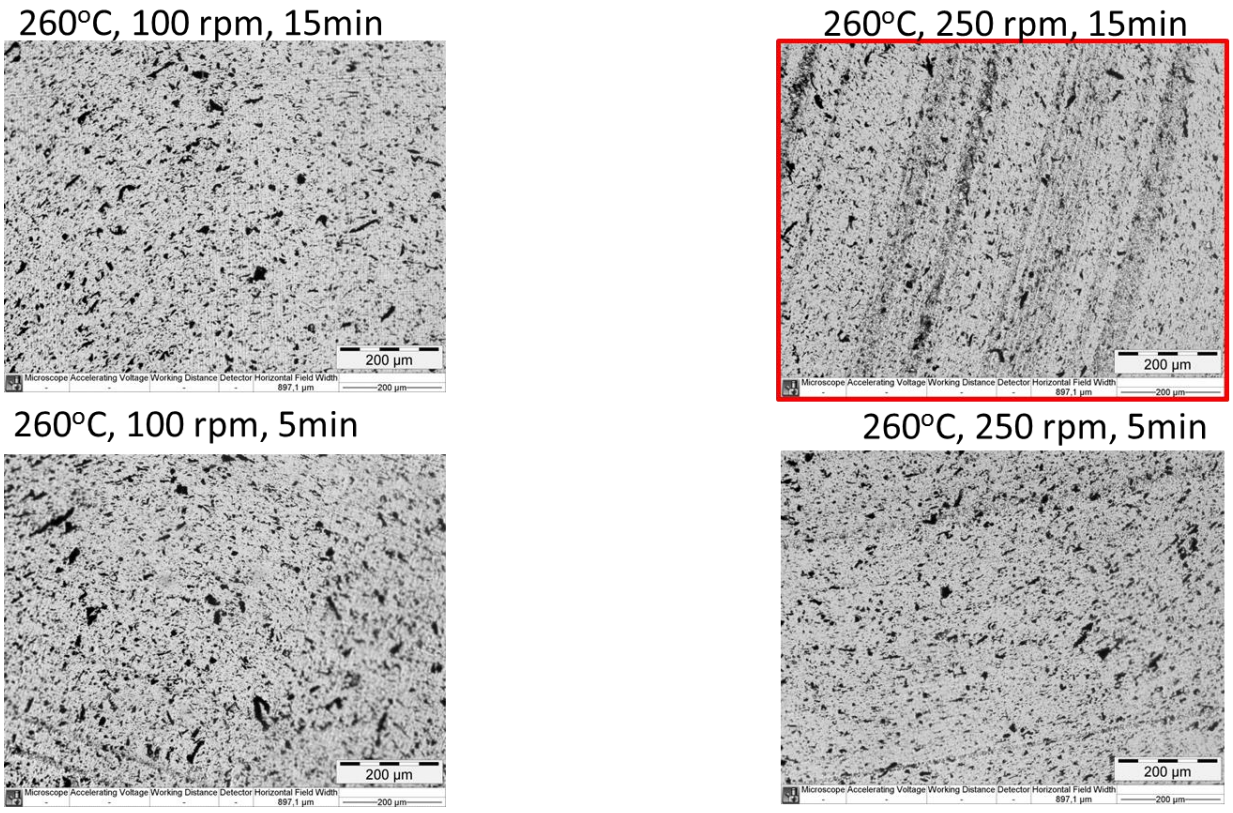
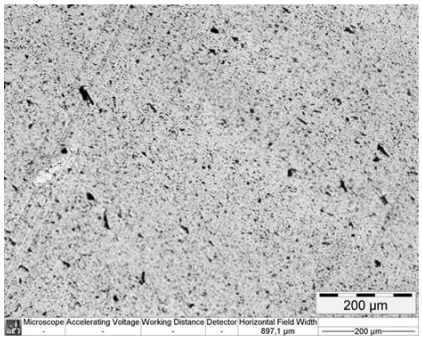
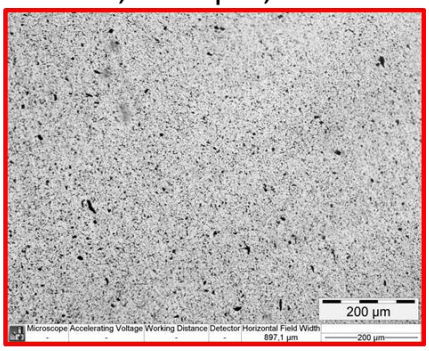


Figure 3 – (1.68 wt% GnPM-5/PC – premix)

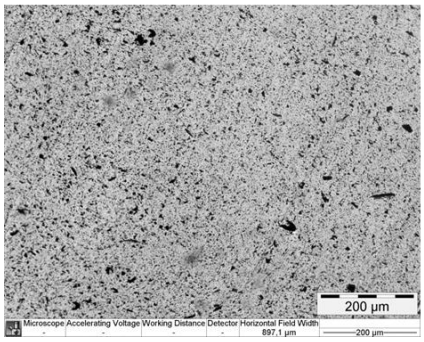
260°C, 100 rpm, 15min



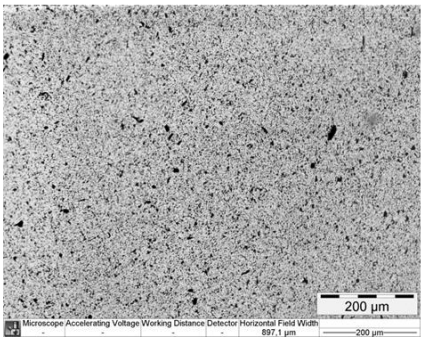

260°C, 250 rpm, 15min




260°C, 100 rpm, 5min




260°C, 250 rpm, 5min



## *Polymer Blends: Premixing Conditions 1: 100 rpm,5 min*

The macro and nanodispersion of these four blend systems were assessed, the former with optical microscopy and the latter with TEM and SEM. The optical microscopy (Fig. 4) clearly indicates a difference in agglomerate shape between the graphene containing samples and the reference containing CNTs. The reference agglomerates are much more spherical in shape than the graphene agglomerates, which are highly irregular. Optically, the graphene agglomerates appear to be the smallest in PC-premixed blend, slightly larger in the SAN-premixed blend, and the largest in the single step blend. Single step blending would be expected to yield larger agglomerates since it only involves a single physical exfoliation step for the graphene. SEM imaging for all three graphene samples shows a clear size discrepancy between the graphene agglomerates and the polymer phases. This is especially noticeable in the single step blend system where SEM seems to indicate that the graphene is neither localized in the PC nor SAN phase. When premixed in PC, the graphene appears to remain within the PC phase, when assessed via SEM and TEM. Graphene was also premixed in SAN in order to assess the transfer kinetics of graphene from the SAN to the PC phase, much like with CNTs in a previous study.[5] The size discrepancy between the agglomerates and the phases seemed to hinder the graphene transfer altogether, as evidence by TEM and SEM imagery.

Figure 4 – GnPM-5(1wt%)/PC(60wt%)/SAN(40wt%)

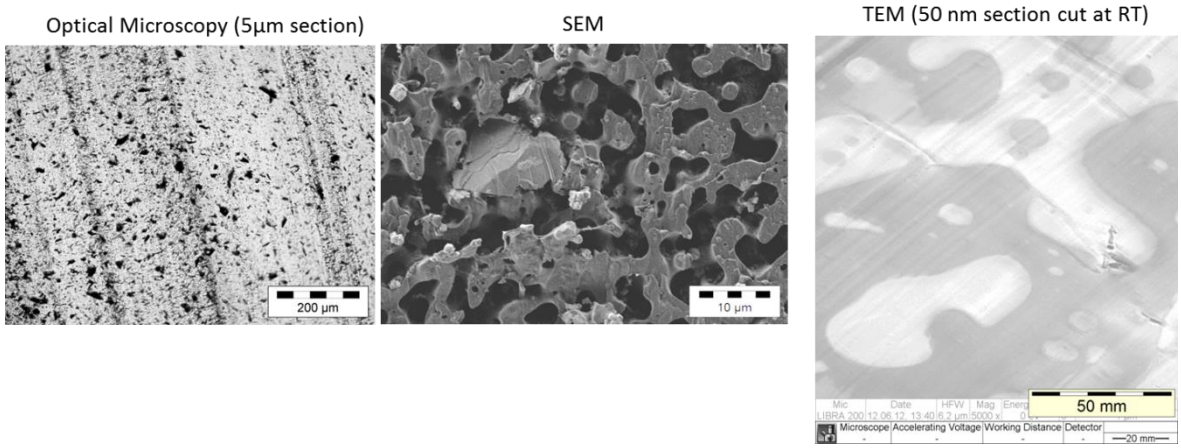


Figure 5 - MWCNT (1wt%) / PC(60wt%)/SAN(40wt%)

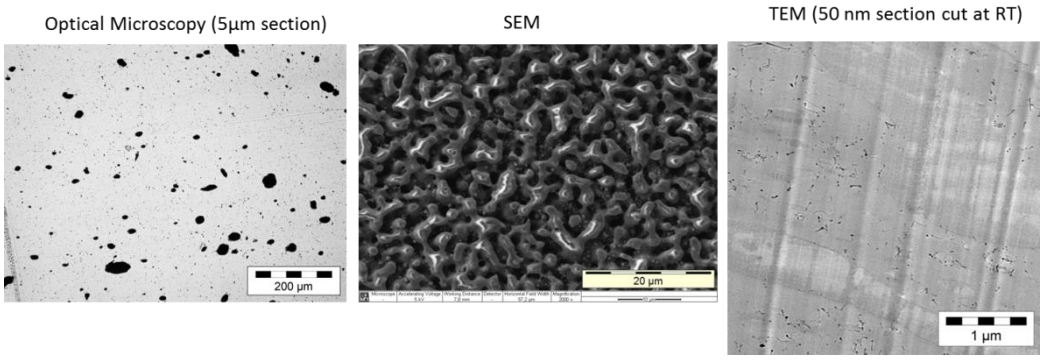



Figure 6 - [GnPM-5(1.68 wt%)/PC (60wt%)premix1a]/SAN(40wt%)

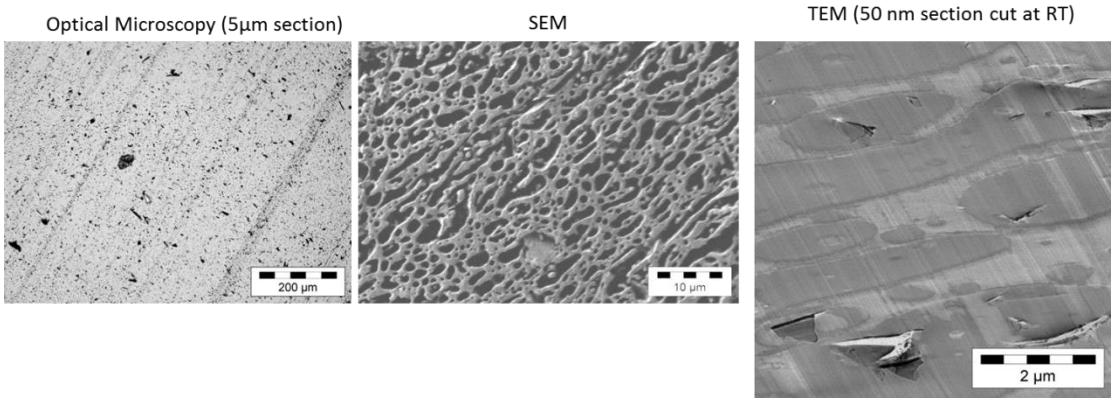
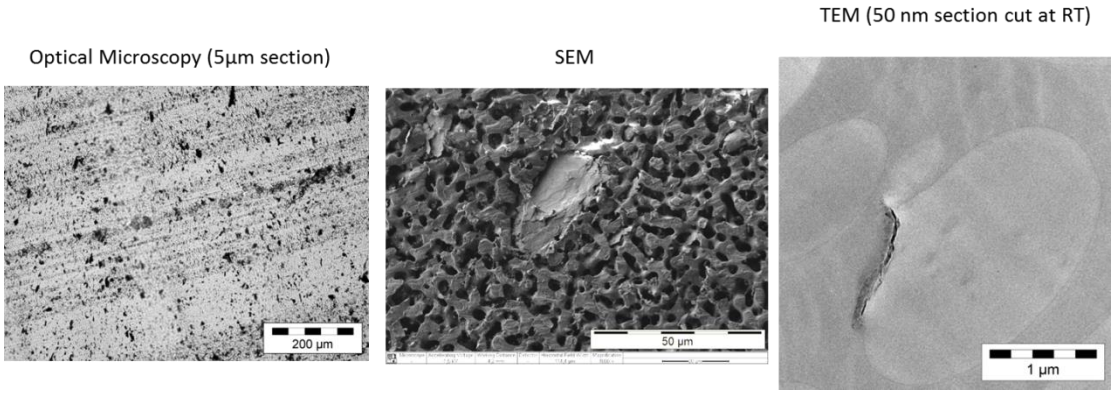
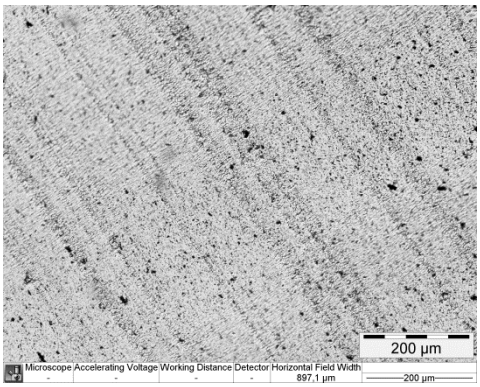
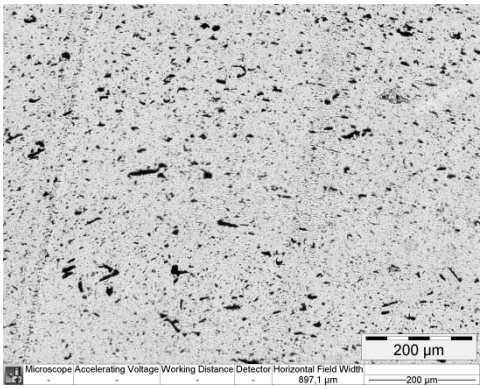
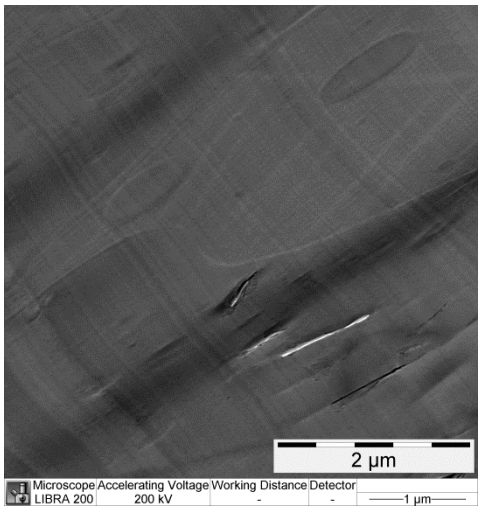
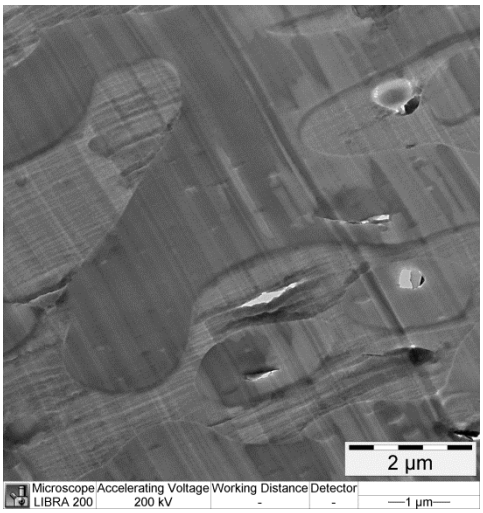



Figure 7 -[GnPM-5(2.53 wt%)/SAN(40wt%) premix1b]/PC (60wt%)



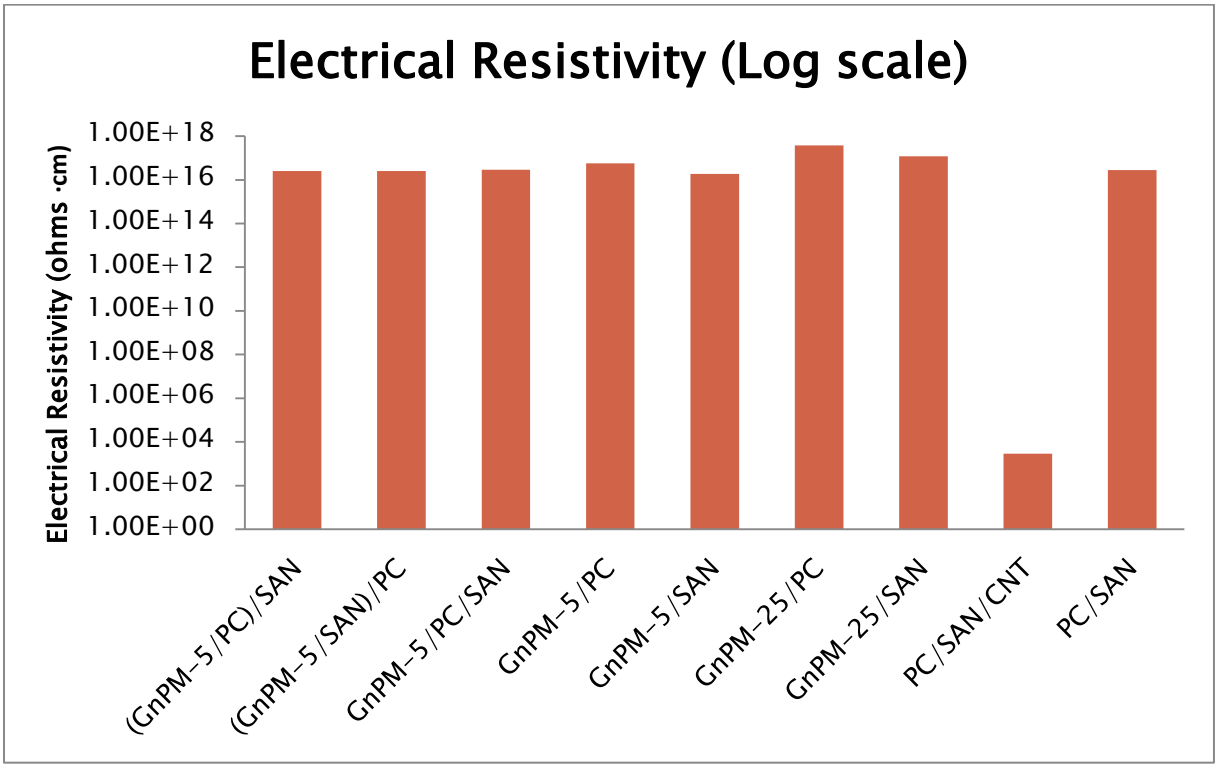
## *Polymer Blends: Premixing Conditions 2: 250 rpm,15 min*

The macro and nanodispersion of these two blend systems were assessed. The former was assessed with optical microscopy and the latter with TEM. The optical microscopy clearly indicates a difference in agglomerate size between the SAN-premixed and PC-premixed samples. The former has visibly larger agglomerates than the latter. TEM clearly indicates that the PC-premixed sample retained the greater part of its graphene agglomerates within a single phase. We speculate that this preferred phase is PC and therefore need to further investigate the elemental make-up of this phase using other spectroscopic techniques. TEM indicates that the SAN-premixed sample contained graphene which was distributed among both visible phases. This implies that there is a phase transfer occurring, which further bolsters the claim that the graphene prefers to reside in the PC phase. This transfer is enabled due to the reduced agglomerate size resulting from the increased speed and time.

| | [GnPM-5(1.68wt%)/PC(60wt%)premix]/SAN(40wt%) | [GnPM-5(1.68wt%)/SAN(60wt%)premix]/PC(40wt%) |
|---|---|---|
| Optical Microscopy |  |  |
| TEM |  |  |

## *Electrical Resistivity Measurements*

Electrical resistivity measurements were conducted on all 1wt% graphene homopolymer samples as well as on polymer blend systems (premix conditions 1), CNT reference, and a non-filled PC/SAN blend. All measurements indicated that all samples were highly insulating excluding the CNT reference. *See appendix for raw data.*



# VI. Conclusion:

This study involved the qualitative characterization of the dispersion of graphene nanoplatelets in various PC or SAN homopolymer and PC/SAN polymer blend systems. Graphene nanoplatelet size, homopolymer type, mixing duration, and screw speed were varied in order to assess their effect on graphene's nano and macrodispersion. Use of smaller graphene nanoplatelets showed improved macrodispersion via optical microscopy in all homopolymers. Mixing with PC showed better dispersion than that seen with SAN. Different blending techniques were also investigated in order to look at phase localization as well as dispersion. Premixing the smallest graphene nanoplatelets (5µm diameter) into PC before blending with SAN produced optimal dispersion as well as resulted in graphene localization in the PC phase. Premixing in SAN resulted in graphene nanoplatelets which were hindered from transferring from SAN to PC. This is explained by the size discrepancy between the graphene agglomerates and the co-continuous polymer phases. These blend systems were compared to CNT infused PC/SAN blends in order to demonstrate the irregularity of the shape of the graphene agglomerates. Different mixing conditions were also explored with homopolymer mixtures with graphene which are to be used in further blending with the partner polymer. SAN showed little visible differences in graphene agglomerate size or dispersion throughout the regime changes. PC showed a clear improvement in both factors when subjected to the longest mixing times and screw speeds. The PC and SAN premixtures subjected to the longest mixing times and screw speeds were then used in creating blend systems with 1wt% graphene. The use of a PC premixture proved to create optimally dispersed graphene with smaller agglomerates. PC/SAN/graphene blends created under various techniques as well as homopolymer/graphene mixtures were tested for electrical resistivity and compared to a CNT infused PC/SAN blends. All graphene containing samples proved to be extremely resistant as opposed to the relative conductive nature of the CNT containing sample.

# VII. Outlook:

Further work needed in order to expand upon these results will include varying other mixing parameters, changing the chemical activity of the graphene, use different filler types , changing the type of polymers used, and using spectroscopic techniques to further characterize the morphology of the samples. Mixing temperature could be increased in order to lower the viscosity of the polymer systems and therefore aid in the exfoliation of the graphene. Polymers with lower inherent viscosities could be used to the same effect. The graphene itself could be chemically modified in order to enhance dispersion. It would be interesting to compare graphene nanoplatelets to expanded graphite, carbon black, and carbon nanotubes in order to truly assess the advantages and disadvantages of using this particular carbon filler. XPS could be used to determine the identity of each polymer phase in a blend system. And finally, we can begin to make more applicable characterizations of the samples by expanding our scope of assessments to include mechanical and further electrical testing.

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# IX. Appendix:

Appendix Fig. 1 – Electrical Resistivity

| | Sample | Resistivity 1 (ohms · cm) | Resistivity 2 (ohms · cm) | Mean Resistivity (ohms · cm) | Standard Deviation |
|---|---|---|---|---|---|
| | (GnPM-5/PC)/SAN | 2.38E+16 | 2.66E+16 | 2.52E+16 | 2.00111E+15 |
| | (GnPM-5/SAN)/PC | 2.40E+16 | 2.65E+16 | 2.52E+16 | 1.72534E+15 |
| | GnPM-5/PC/SAN | 2.84E+16 | 3.04E+16 | 2.94E+16 | 1.37886E+15 |
| | GnPM-5/PC | 6.07E+16 | 5.16E+16 | 5.62E+16 | 6.46296E+15 |
| | GnPM-5/SAN | 1.73E+16 | 2.03E+16 | 1.88E+16 | 2.12132E+15 |
| | GnPM-25/PC | 3.45E+16 | 7.13E+17 | 3.74E+17 | 4.79878E+17 |
| | GnPM-25/SAN | 1.32E+17 | 1.09E+17 | 1.21E+17 | 1.61927E+16 |
| ***Strip measurement taken*** | PC/SAN/CNT | 2.86E+03 | N/A | 2.86E+03 | 0 |
| | PC/SAN | 2.69E+16 | 2.99E+16 | 2.84E+16 | 2.07182E+15 |

Appendix Fig. 2 – Raw Material Weightings and Mixing Force Measurements

## *Comparison of xGnP M-5 and xGnP M-25*

1. GnPM-5(1wt%) / PC : .1499g GnPM-5, 14.253g PC / Start Force: 4500N
2. GnPM-25 (1wt%) /PC : 0.144g GnPM-25, 14.255g PC
3. GnPM-5(1wt%) / SAN: .1477g GnPM-5, 12.834g SAN /Start Force: 1900N, End Force: 1900N
4. GnPM-25(1wt%) / SAN: 0.1479g GnPM-25, 12.8226g SAN / Start Force: 2600 N, End Force: 2200N

## *Comparison of different melting conditions with xGnP M-5*

1. (1.68 wt% GnPM-5/PC – premix) : 260°C, 250 rpm, 5 min: .2439 g GnPM-5, 14.279g PC
2. (1.68 wt% GnPM-5/PC – premix) : 260°C, 250 rpm, 15 min: .247g GnPM-5, 14.285g PC
3. (1.68 wt% GnPM-5/PC – premix) : 260°C, 100 rpm, 15 min: .241g GnPM-5, 14.269g PC
4. (1.68 wt% GnPM-5/PC – premix) : 260°C, 100 rpm, 5 min: .247g GnPM-5, 14.287g PC
5. (2.53 wt% GnPM-5/SAN – premix) : 260°C, 250 rpm, 5 min: .326g GnPM-5, 12.808g SAN / Start Force: 1998N, End Force: 1890N

6. (2.53 wt% GnPM-5/SAN – premix) : 260°C, 250 rpm, 15 min: .3255g GnPM-5, 12.807g SAN
7. (2.53 wt% GnPM-5/SAN – premix) : 260°C, 100rpm, 15 min: .3250g GnPM-5, 12.806g SAN
8. (2.53 wt% GnPM-5/SAN – premix) : 260°C, 100rpm, 5 min: .328g GnPM-5, 12.812g SAN

## *Mixing Conditions 1: 5min, 100rpm*

1. GnPM-5(1wt%)/PC(60wt%)/SAN(40wt%): No data available
2. [GnPM-5(1.68 wt%)/PC (60wt%)premix1a]/SAN(40wt%): 8.368g premix 1a, 5.488g SAN
3. [GnPM-5(2.53 wt%)/SAN(40wt%) premix1b]/PC (60wt%): 5.624g premix1b, 8.239g PC/ Start Force: 2515N, End Force:2375N
4. MWCNT (1wt%)/PC(60wt%)/SAN(40wt%): .1381g MWCNT, 8.218g PC, 5.4795g SAN

## *Premixing Conditions 2: 15 min, 250rpm*

1. _[GnPM-5(1.68 wt%)/PC (60wt%)premix]/SAN(40wt%): .2479g GnPM-5, 14.295g PC, 5.494g SAN / Premixing Forces: [Start: 5578N, End: 5343N] / Blending Forces: [Start:2520N,End:2313N]
2. [GnPM-5(2.53 wt%)/SAN(40wt%) premix]/PC (60wt%): .3298g GnPM-5, 12.8117g SAN, 8.234g PC / Premixing Forces: [2865N,End:1978] / Blending Forces: [Start:1938N,End:1775N]